

Pyrolysis Products of PCBs

by Jaakko Paasivirta,*† Rainer Herzs Schuh,‡ Tarmo Humpi,**
Erkki Kantolahti,** Juha Knuutinen,* Mirja Lahtiperä,*
Risto Laitinen,** Juhani Salovaara,* Juhani Tarhanen*
and Liisa Virkki*

Model compound studies which were previously done for impurities and environmental residues of chlorophenols and for wastes of chlorination processes were extended to the impurities and pyrolysis products of polychlorinated biphenyls (PCBs). Model compounds were commercial products or synthesized and their structures proven by spectroscopic methods. These models were used as analytical reference substances in GC/ECD and GC/MS studies of the pyrolyzed PCB samples. In addition to previously known neutral components like polychlorinated dibenzofurans (PCDFs), chlorophenolic substances, especially polychlorophenols (PCPs) and polychlorinated biphenylols (PCB-OHs) were observed as major pyrolysis products of PCBs. Capacitor fires are suggested to produce in many cases chlorophenols which are major toxic hazards to people.

Introduction

Our laboratory has been working on structural and environmental chemistry of polyhalogenated aromatic compounds since 1973, when we made the first observations of the occurrence of chlorophenols in aquatic food chain samples (1). The first model compound studies, development of trace analysis methods and analyses of environmental samples were done for chlorophenols, catechols, cresols, guaiacols and their derivatives. These compounds were considered important wastes from wood preservation and chlorination processes like chlorobleaching of pulp, chlorodisinfection of water and later also as combustion residues (2-38). 2,3,7,8-TCDD as an important possible co-contaminant was added to our studies in 1976 (38-41).

Other polyhalogenated aromatic compounds containing two or more benzene rings were included to our structure analyses in 1978 in order to monitor impurities of the wood preservative chlorophenol formulations in their preparation and waste treatment (42). Especially, polychlorinated phenoxyphenols (PCPP) were synthesized by us to complete the series of these important chlorophenol impurity models (43), which had been started by Nilsson in his Ph.D. thesis (44-46). Recently,

we have studied dimeric polyhalogenated aromatic (PHA) impurities in spent chlorobleaching liquors and pyrolysis products of PCBs by gas chromatographic and mass spectrometric analyses and by comparisons with available model compounds. Observations on the pyrolysis products of PCBs are described in this paper.

Components Studied

Structures and commonly used abbreviations of the names of neutral components and pyrolysis products of PCBs are shown in Figure 1 and those of the possible phenolic pyrolysis products in Figure 2.

Structure analyses of the toxic pyrolysis products of PCBs have been intensively made since chick edema disease was experienced in the US broiler industry in 1957 and caused deaths of millions of chickens (47). A major toxic product was determined 1969 by crystallography to be 1,2,3,7,8,9-hexa CDD (48). PCDFs and PCNs were observed in commercial PCBs in 1970 (49). In 1968 more than 1000 persons in Japan were poisoned by a rice oil (Yusho oil) contaminated by PCBs used as a heat transfer medium, and PCDFs were found as main toxic factors (50). Polychlorinated terphenyls (PCTs) which had been found in PCB were also identified as environmental poisons in 1977 (51). The importance of combustion as source of such toxic and persistent materials was exposed in 1977, when PCBs among other chlorohydrocarbons (52) and also PCDDs and PCDFs

*Department of Chemistry, University of Jyväskylä, Kyllikinkatu 1-3, SF-40100 Jyväskylä 10, Finland.

†2Section Chemie, Karl Marx Universität, Leipzig, DDR.

**Research Centre of Defence Forces, SF-34111 Lakiala, Finland.

†Author to whom requests should be sent.

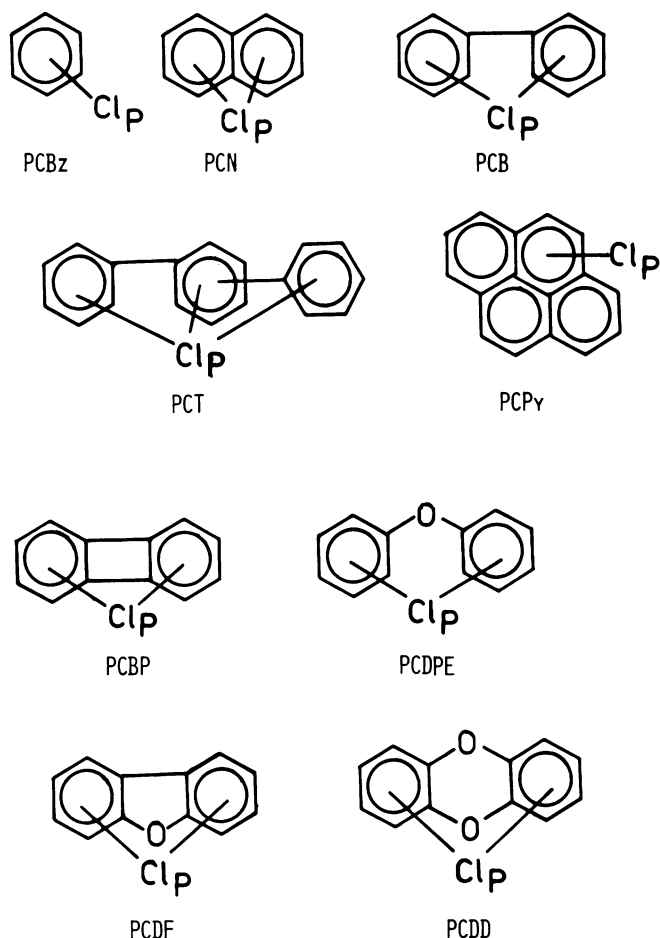


FIGURE 1. Neutral compounds and pyrolysis products: (PCBz) polychlorinated benzenes; (PCN) polychlorinated naphthalenes; (PCB) polychlorinated biphenyls; (PCT) polychlorinated terphenyls; (PCPy) polychlorinated pyrenes; (PCBP) polychlorinated biphenylenes; (PCDPE) polychlorinated diphenyl ethers; (PCDF) polychlorinated dibenzofurans; (PCDD) polychlorinated dibenzodioxins.

(53) were found in fly ash and flue gases of municipal incinerators.

Experimental pyrolysis of PCB was reported in 1978 by Morita, Nakagawa and Rappe (54) and more completely by Buser and his co-workers (55–57). PCDFs were found as main toxic products at 550–650°C; formation of PCDDs and polychlorinated benzenes (PCBz) was also reported. Consequently, the important role of PCDFs in chick edema and Yusho oil poisonings was verified (58). Hexachlorobenzene (HCB) which was detected in PCB pyrolysis (56) has also been demonstrated to be a major product of fast high temperature combustion (degradation) of PCB (59). Polychlorinated diphenyl ethers (PCDPEs) have also been found in PCBs and in combustion products (44,55,60). GC/MS analyses of municipal incinerator fly ash (61) confirm the existence of the neutral PCB pyrolysis products mentioned above, e.g., different PCBz and PCN compounds and, in addition, polychlorinated benzofurans and tetrachlorobiphenylene (TCBP).

Formation of PCDFs and other neutral PCB pyrolysis products in fire accidents has been monitored (62–64). In addition to product types mentioned above, PCBP and polychlorinated pyrenes (PCBP_y) (Fig. 1) have been reported to be formed in PCB fires (64), and 2,3,6,7-TCBP has also been studied as an TCDD-type super-poison (65).

It is obvious that chlorophenolic compounds (Fig. 2) are formed in PCB pyrolyses, but their structure analyses have been reported only from chlorophenol formulations and wastes (42–44) and from incinerator wastes (53,61). Model compound syntheses, spectroscopy and chromatography have been reported for polychlorophenols (PCP) and catechols (PCC) (3–5,7,8, 11,14,16–18,23,31,32,34), for polychlorinated phenoxyphenols (PCPP) (43–46) and for polychlorinated biphenylols (PCB-OH) and biphenyldiols (PCB(OH)₂) (66,67). Polychlorinated dibenzofuranols (PCDF-OH), phenoxydiphenyldiols [PCPB(OH)₂] and phenoxyphenoxyphenols (PCPPP) were only detected in chlorophenol formulations and wastes by GC/MS (42).

Experiments

Open Flame Pyrolysis

A 120-mg portion of a PCB mixture (Aroclor 1254) in hexane was adsorbed on Whatman #1 filter paper; after

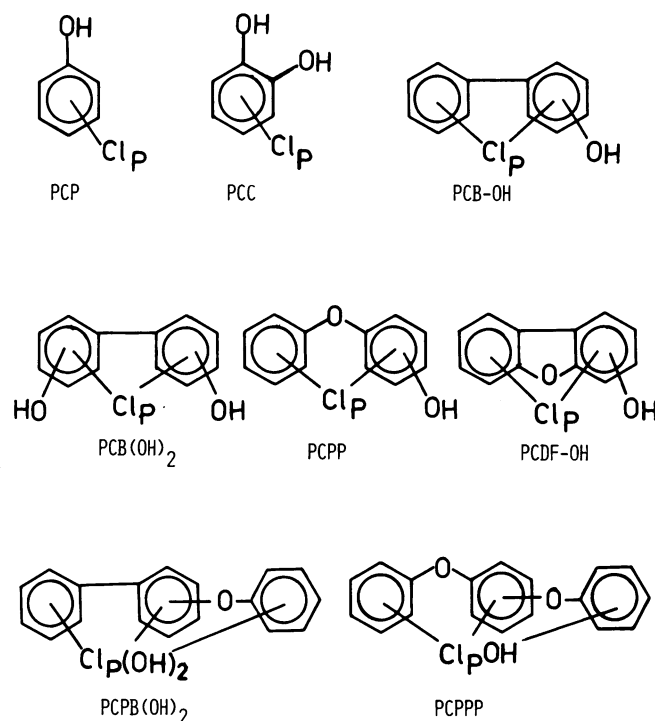


FIGURE 2. Phenolic pyrolysis products and impurities of chlorophenols: (PCP) polychlorophenols; (PCC) polychlorocatechols; (PCB-OH) polychlorinated biphenylols; (PCB(OH)₂) polychlorinated biphenyl diols; (PCPP) polychlorinated phenoxyphenols; (PCDF-OH) polychlorinated dibenzofuranols; (PCPB(OH)₂) polychlorinated phenoxydiphenyl diols; (PCPPP) polychlorinated phenoxyphenoxyphenols.

evaporation of the solvent the paper was burned with a bunsen flame at 300–400°C in 5 minutes. Smoke and gases were collected with suction via funnel through a tube containing 1 g of XAD7/XAD4 adsorbent mixture (1:1).

Quartz Tube Pyrolysis

The Hamilton multipurpose sampling system was used. A sample of the PCB mixture (Aroclor 1254) was weighed into a 5 cm quartz tube of 0.8 mm internal diameter which was then stoppered with quartz wool and put into a quartz pyrolysis tube of 4 mm internal diameter. An air stream (40 mL/min) was started, and pyrolysis was done in the 20 cm heating zone at 500, 600 and 700°C followed by heating in the 10 cm tube zone at 300°C. The adsorption tube was then filled with 1 g of XAD7/XAD4 (1:1) mixture. Pyrolysis time was 3 seconds. Three successive samples of about 30 mg were pyrolyzed and all products were trapped in the same adsorption tube.

Fractionation of the Pyrolysis Products

Pyrolysis products were desorbed from the XAD mixture by eluting with 20 mL of an acetone–hexane 1:1 (v/v) mixture. The evaporated eluate was dissolved in 25 mL of hexane and shaken in a separatory funnel with 50 mL of 0.1 M K₂CO₃ water solution. The separated water phase was washed five times with 20 mL of hexane, and the organic phases were combined to form the neutral product fraction.

The water phase was shaken with 1 mL of acetic acid anhydride and allowed to stand for 5 min. The acetate derivatives of phenols thus formed were taken into 20 mL of hexane by shaking. The hexane solution was used for GC/MS and GC/ECD analyses of phenolic fraction.

Extra solvent was evaporated from the neutral product fraction, and the residual 2 mL solution was shaken with 2 mL of concentrated sulfuric acid and then fractionated in an alumina microcolumn following the procedure of Buser (68) by eluting PCBs with 2% methylene chloride in hexane (fraction I) and PCDFs and PCDDs with 50% methylene chloride in hexane (fraction II). The latter fraction was investigated by GC/MS and GC/ECD.

Analysis of the Capacitor Fire Fumes

Samples of carbon filter containing fire fumes were weighed and Soxhlet-extracted with toluene for 24 hr. The phenol fraction was taken in 0.2 N NaOH by two funnel extractions, washed with hexane and neutralized with dilute sulfuric acid to pH 7. Potassium carbonate was added to 0.1 M solution, and the procedure continued with acetic anhydride as in the case of pyrolysis products (see above). The hexane, in addition to PCB and other neutral impurities, removed 3-, 4- and 5-chlorophenols which made quantitation a problem. (GC/MS

in Figure 8 is from a sample washed eight times, and thus only a small part of the original 3CP, 4CP and 5CP remains in the phenolic fraction.) The combined toluene and hexane solutions were evaporated and handled for analysis of neutral components as in the case of the pyrolysis products (see above).

GC/MS Analyses

A Finnigan model MAT 212 system was used. The GC column was a 20 m long, 0.3 mm diameter quartz capillary coated with SE-54 to film thickness 0.4 µm. Both chlorophenol acetate and neutral fraction (fraction II) were injected with 1:10 split at 260°C. Helium was used as carrier gas 1 mL/min. Temperature program of 60° + 10°C/min to 260°C was used. An open split and quartz capillary connection led to the ion source having a temperature of 200°C where 70 V electron impact was applied. Continuous scans at the mass number range 50–550 were run at a speed of 2.3 sec per full scan; mass spectra were collected in data storage using 1000 × resolution (10% valley).

GC/ECD Analyses

A Micromat HRGC 412 two-column system was used. Both columns were 25 m long, 0.3 mm diameter quartz capillaries. One column was coated with SE-54 and the other with OV-1701 to a film thickness of 0.25 µm. Injection with 1:10 split was applied at 275°C. The carrier gas was helium (1 mL/min) and the makeup gas to the ⁶³Ni EC detectors was argon-methane, 95:5 (v/v) at a rate of 18 mL/min. Temperature programs used were for chlorophenol acetate fraction 100°C + 4°C/min to 250°C and for the neutral fraction (fraction II), 60°C + 10°C/min to 280°C.

Identification

Structures of the components were deduced primarily from the mass chromatograms of selected ions precalculated for each type (Figs. 1 and 2) and each number (P) of chlorine atoms. After detection of a peak for the selected ion, the corresponding mass spectrum was reconstructed and the structure of the component verified. If model compounds of the type were available, they were chromatographed by GC/MS and GC/ECD exactly under the same conditions as actual samples. Retention times at each column and MS comparison gave a firm identification of the structure of the component. The minor components (which gave mass chromatogram peaks of too low intensity of *M/Z* of their ions to be recognized) could in some cases be detected from the total mass spectra of major components as clearly resolved extra ion clusters ("impurity peaks").

Quantitation

A large number of chlorophenolic and a few PCDF and PCDD model compounds (4CDF, 2 × 4CDD, 8CDF

Table 1. Compounds detected by GC-MS and identified by comparison with model compounds in the phenolic fraction of PCB pyrolysis product and capacitor fire fumes.

Scan No.		Type detected	Structure identified	Structure No.
F. 3,4	F. 8			
119	121	1CP	2-Chlorophenol	1
130	132	1CP	3-Chlorophenol	2
132	134	1CP	4-Chlorophenol	3
158		2CP	2,6-Dichlorophenol	4
163	166	2CP	2,4-Dichlorophenol	5
163		2CP	2,5-Dichlorophenol	6
166		2CP	3,5-Dichlorophenol	7
172		2CP	2,3-Dichlorophenol	8
179		2CP	3,4-Dichlorophenol	9
189	192	3CP	2,4,6-Trichlorophenol	10
202		3CP	2,3,6-Trichlorophenol	11
204		3CP	2,3,5-Trichlorophenol	12
206	207	3CP	2,4,5-Trichlorophenol	13
206		2CDihydroxybenzene		21
217		3CP	2,3,4-Trichlorophenol	14
220		3CP	3,4,5-Trichlorophenol	15
237		4CP	2,3,5,6-Tetrachlorophenol	16
238	238	4CP	2,3,4,6-Tetrachlorophenol	17
251		4CP	2,3,4,5-Tetrachlorophenol	18
279	279	5CP	Pentachlorophenol	19
	297	2CB-OH		31
	308	2CB-OH		32
	311	2CB-OH		33
	312	3CB-OH		34
	314	2CB-OH		35
	317	2CB-OH		36
	323	2CB-OH		37
324		4CDihydroxybenzene	Tetrachlororesorcinol	22
	326	2CB-OH		38
	326	3CB-OH		39
	329	2CB-OH		40
	331	2CB-OH		41
	331	3CB-OH		42
332		4CDihydroxybenzene	Tetrachlorohydroquinone	23
	334	2CB-OH		43
	334	2CB-OH		44
	336	3CB-OH		45
	340	3CB-OH		46
	344	3CB-OH		47
	346	3CB-OH		48
344	348	3CB-OH		49
	352	3CB-OH		50
	353	4CB-OH		51
357		4CB-OH		52
	364	4CB-OH		53
364		4CB-OH		54
366		4CB-OH		55
373		5CB-OH		56
376		4CB-OH		57
381		4CB-OH		58
384		4CB-OH		59
384		5CB-OH		60
386		4CB-OH		61
386		5CB-OH		62
390		4CB-OH		63
390		5CB-OH		64
393		5CB-OH		65
396		5CB-OH		66
396		6CB-OH		67
397		5CB-OH		68
400		5CB-OH		69
406		6CB-OH		70
415		6CB-OH		71
416		6CB-OH		72
420		5CB-OH		73

Table 1. (continued)

Scan No.		Type detected	Structure identified	Structure No.
F. 3,4	F. 8			
422		6CB-OH		74
424		5CB-OH		75
429		6CB-OH		76
437		6CB-OH		77

^aScan numbers refer to mass chromatograms in Figs. 3, 4 and 8.

Table 2. Relative amounts of the major phenolic pyrolysis products formed from PCB (Aroclor 1254) in quartz tube pyrolysis in air stream at 500, 600 and 700°C and in carbon filter from a capacitor fire.

	Pyrolysis 500°C	Pyrolysis 600°C	Pyrolysis 700°C	Filter
1CP	0.5	2.9		0.9
2CP	8.4	12.6		13.8
3CP	39.2	61.8		26.7
4CP	36.4	18.9		56.5
5CP	15.4	3.6		2.0
PCP	100	100		100
1CB-OH	0.0	0.0	0.0	1.3
2CB-OH	0.0	0.0	0.0	63.2
3CB-OH	16.6	1.5	4.6	38.8
4CB-OH	52.4	42.3	68.5	0.6
5CB-OH	31.0	49.0	26.9	0.0
6CB-OH	0.0	7.2	0.0	0.0
PCB-OH	100	100	100	100
PCP/PCB-OH	9.5	2.81	0.0	200 ^a

^aLarge variation between samples from different parts of the carbon filter and dependence on hexane washes makes this number inaccurate.

and 8CDD) in our laboratory were used as external standards and in some cases weighed and added to the analysis mixtures to obtain comparison of the GC/MS and GC/ECD peak intensities. While, however, identical models were absent for most dimeric components in the complex product mixtures, response of an "average model compound" was taken as quantitation standard for each structure type. 2,4,5-Tribromophenol was used as response standard compound for both monomeric and dimeric chlorophenols, and 1,2,3,4-tetrachlorodibenzo-*p*-dioxin was used for neutral dimers. Due to difficulties in fractionation and cleanup operations, the absolute amounts could, however, only be estimated to an accuracy of one order of magnitude.

Relative amounts within compounds types could be obtained more precisely from the present data. From reconstructed mass chromatograms the areas of the M-42 ions of the phenolic components and the M-ions of the neutral components were compared. In this way, ratios of 74 product components within PCP and PCB-OH groups listed in Table 1 were calculated, and the results are presented in Table 2. Also ratios of the main neutral pyrolysis products within groups PCDF and PCDD were calculated, and the results are collected in Table 3.

Table 3. Relative amounts of the major neutral pyrolysis products formed from PCB (Aroclor 1254) in quartz tube pyrolysis in air stream at 500, 600 and 700°C and in carbon filter from a capacitor fire.

	Pyrolysis 500°C	Pyrolysis 600°C	Pyrolysis 700°C	Filter
1CDF	0.1	0.3	0.01	51.8
2CDF	13.7	12.8	5.2	44.3
3CDF	38.8	39.3	29.4	3.9
4CDF	40.0	35.9	48.7	0.0
5CDF	7.4	11.0	15.1	0.0
6CDF	0.0	0.8	1.5	0.0
PCDF	100	100	100	100
2CDD	17.2	0.7	4.6	
3CDD	10.0	18.4	13.6	
4CDD	72.9	57.0	66.3	
5CDD	0.0	24.1	17.4	
PCDD	100	100	100	
PCDF/PCDD	205	28	137	

Results and Discussion

Products of the first experiment, open flame (Bunsen) pyrolysis at 300–400°C were analyzed by GC/ECD using model compounds and only the monomeric chlorophenols (PCPs) were sufficiently well resolved to be identified and quantified. As a result, the following production of PCP groups based on the original amount of Aroclor 1254 was measured: 1CP, 4 ppm; 2CP, 3 ppm; 3CP, 2 ppm. GC/MS also detected PCB-OHs; the estimated amounts were: 2BC-OH, 0.1 ppm; 3CB-OH, 0.2 ppm; 4CBOH, 0.2 ppm; 5CB-OH, 0.05 ppm; 6CB-OH, 0.01 ppm.

GC/MS and GC/ECD chromatograms of the phenolic product fractions from pyrolyses and capacitor fires are illustrated in Figures 3–8; qualitative analysis (detection and identification) results of this fraction are given in Table 1. Reconstructed MIS gave ratios of the main components which are collected in Table 2. Absolute amounts could be estimated reasonably only from the filter sample when the phenol fraction was washed eight times with hexane: 20.6 ppm PCP and 12.8 ppm PCB-OH were found in the filter. The real amount of PCP must have been much higher, but hexane has removed most of PCP. 2,4,6-Trichlorophenol and 2,3,4,6-tetrachlorophenol (structure nos. 10 and 17) were especially abundant in nonwashed filter sample.

Neutral fractions I were only preliminarily investi-

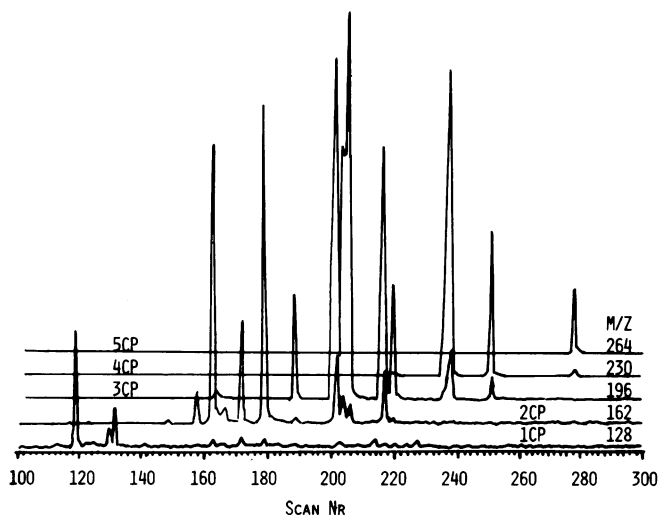


FIGURE 3. Mass chromatograms of the acetylated phenolic fraction of the product of pyrolysis of PCB mixture Aroclor 1254 at 600°C. *M/Z* values of the traces were selected to correspond M-42 fragment of monomeric chlorophenol (PCP) acetates. The verified (from total mass spectra and by RT-comparison with model compounds) PCPs are listed in Table 1.

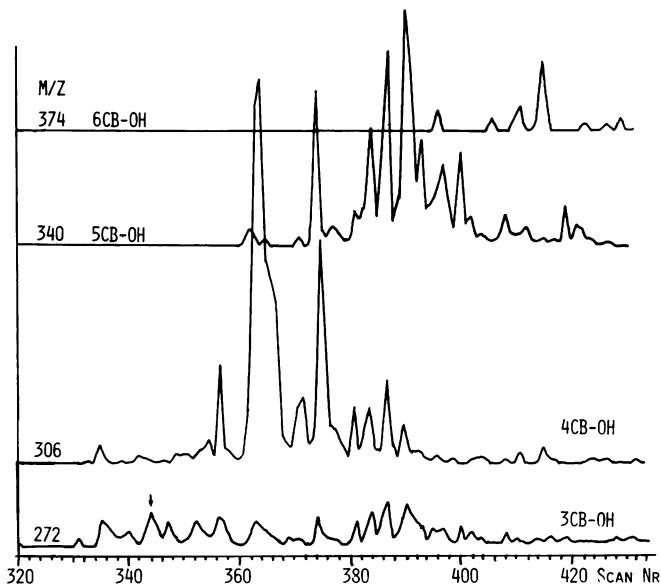


FIGURE 4. Mass chromatograms of the acetylated phenolic fraction of the product of pyrolysis of PCB mixture Aroclor 1254 at 600°C. *M/Z* values of the traces were selected to correspond M-42 fragment of polychlorinated biphenyl (PCB-OH) acetates. The only observable peak from real 3CB-OH (scan 344) is marked by an arrow. The verified (from total mass spectra) PCB-OHs are listed in Table 1.

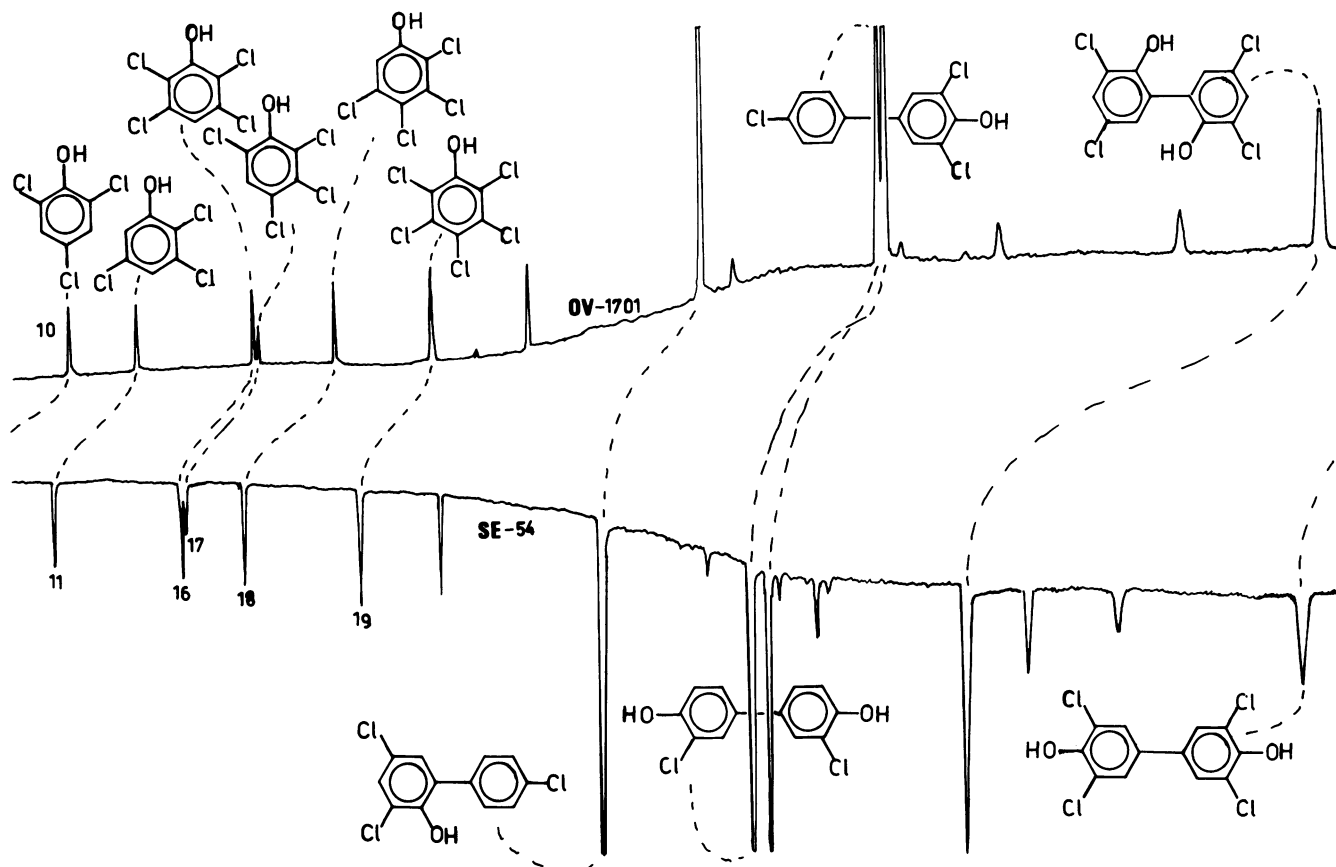


FIGURE 5. Two-channel gas chromatogram of an acetylated mixture of PCP, PCB-OH and PCB(OH) model compounds. Micromat HRGC instrument. For conditions see experimental part.

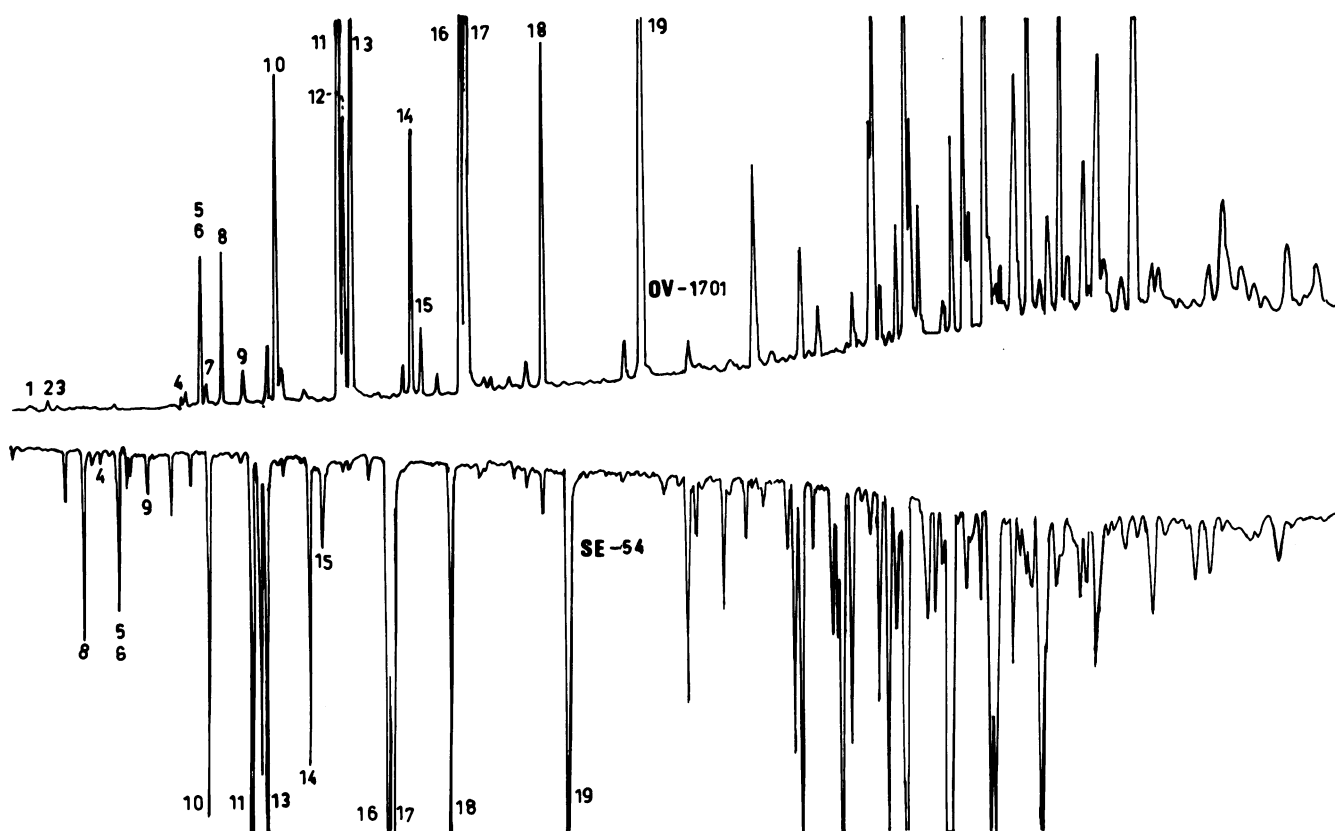


FIGURE 6. Two-channel gas chromatogram of the acetylated phenol fraction of the 500°C pyrolysis product of PCB Aroclor 1254. Micromat HRGC instrument. For conditions see experimental part.

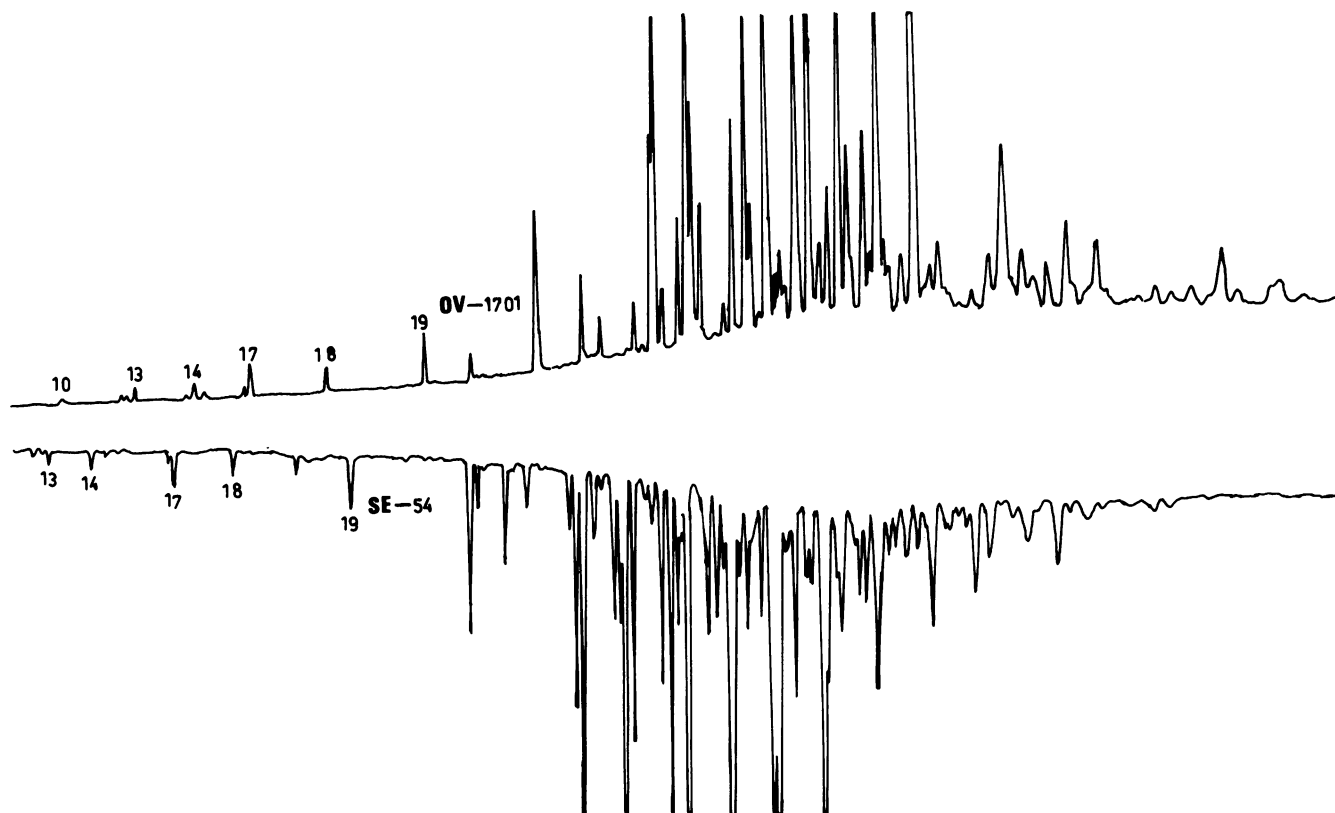


FIGURE 7. Two-channel gas chromatogram of the acetylated phenol fraction of the 700°C pyrolysis product of PCB Aroclor 1254. Micromat HRGC instrument. For conditions see experimental part.

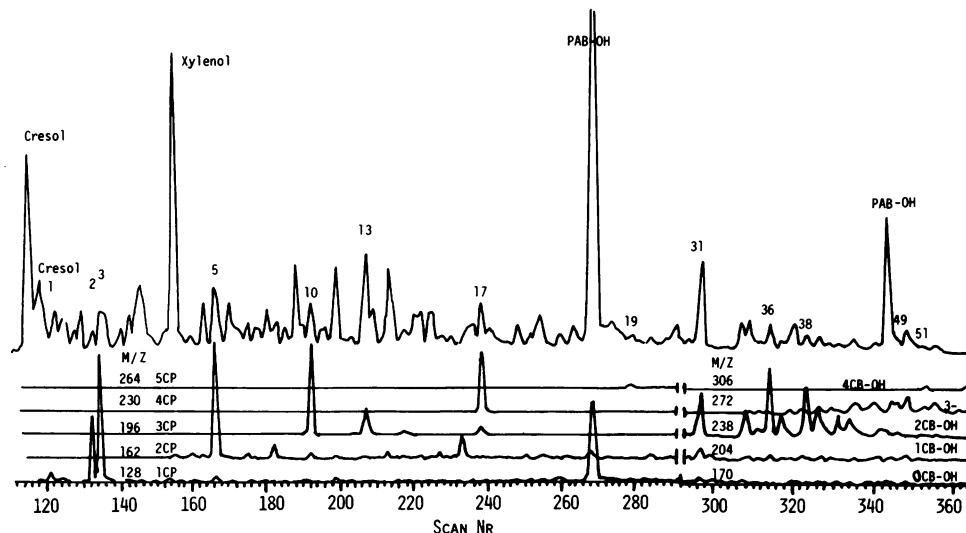


FIGURE 8. Mass chromatograms of the acetylated phenolic fraction washed eight times with hexane of the contents of the carbon filter which had been used to collect fumes in a capacitor fire (Enso 3.8.1982). *M/Z* values of the traces were selected to correspond M-42 fragment of polychlorinated phenol (PCP) or biphenylol (PCB-OH) acetates. The verified (from total mass spectra) PCPs and PCB-OHs are listed in Table 1. Polyalkylbenzenoid (PAB-OH) peaks correspond to MS of di-*tert*-butylethylphenol (scan 268) and pentamethylbiphenylol (scan 343).

gated by GC/ECD and GC/MS. PCBs from the pyrolysis experiments was very similar to the original Aroclor 1245. In 700°C pyrolysis, formation of polychlorobenzenes (PCBz) was observed. Fraction I from filter showed low-chlorinated PCBs which were obscured by many peaks, of which a great part represents nonchlorinated compounds. Neutral fraction I of the 600°C pyrolysis also contained chlorinated naphthalenes which were estimated by MS to appear in the ratios 2CN, 0.25%; 3CN, 36.4%; 4CN, 63.36% (when PCN is 100%). Still very much lower amounts of 1CPy and 2CPy were detected in neutral fraction I of the pyrolysis at 600°C.

GC/MS chromatograms of the neutral fraction II were similar to those published in earlier papers (55–58, 64), in reconstructed mass chromatograms from fraction II run with selected ions, however, large peaks with high S/N ratio were obtained from PCDFs (major product components) only. On reconstructing total mass spectra, some PCDD, PCN and PCPy component types were also detected. Main neutral dimer structure types found in pyrolyses were (in order of abundance) 3CDF, 4CDF, 2CDF, 4CDD and 5CDD. 1CDF and 6CDF were detected as minor components. In pyrolysis of Aroclor 1254 at 600°C, 0.16% conversion to PCDF and PCDD was estimated, which is somewhat lower but of the same order of magnitude as reported by Buser, Bosshardt and Rappe (56).

Ratios of the main neutral components (from reconstructed MIS) are collected in Table 3. The absolute amounts of PCDF in the Enso filter were also estimated to be 15.8 ppm in carbon. Consequently, chlorinated phenols appear to be an order of magnitude more abundant in capacitor fire products studied here than PCDFs.

Our present finding of high amounts of PCP and PCB-OH in PCB pyrolysis and capacitor fire products and abundant formation of only 1–3CDF in the latter calls

for new toxicological evaluation of the risk components in certain accidents.

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